



TITLE:

Studies on the Syntheses of Organic Fluorescent Compound. (I-II)

AUTHOR(S):

Oda, Ryohei; Yoshida, Zen-ichi

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RIGHT:

- (1) $2\text{CH}_3\text{OCH}_2\text{Cl} \longrightarrow \text{CH}_3\text{OCH}_2\text{OH}_2\text{OCH}_3$ 73% (70°C, 5hrs)
- (2) $2\text{C}_2\text{H}_5\text{OCH}_2\text{Cl} \longrightarrow \text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ 70% (80°C, 5hrs)
- (3) $2\text{C}_4\text{H}_9\text{OCH}_2\text{Cl} \longrightarrow \text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OC}_4\text{H}_9$ 66.6% (150°C, 3hrs)
- (4) $2\text{C}_4\text{H}_9\text{OCH}(\text{Cl})\text{CH}_3 \longrightarrow \text{C}_4\text{H}_9\text{OCH}(\text{CH}_3)\text{CHOC}_4\text{H}_9$ 50.5% (120°C, 5hrs)
- (5) $2\text{C}_4\text{H}_9\text{OCH}(\text{Cl})\text{C}_3\text{H}_7 \longrightarrow \text{C}_4\text{H}_9\text{OCH}(\text{C}_3\text{H}_7)\text{CHOC}_4\text{H}_9$ 54% (110°C, 10hrs)
- (6) $2\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OCH}_2\text{Cl} \longrightarrow \text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$ 41% (150°C, 10hrs)
- (7) $2\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{Cl} \longrightarrow \text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$ 50.5% (140°C, 10hrs)
- (8) $2\text{C}_{12}\text{H}_{25}\text{OCH}_2\text{Cl} \longrightarrow \text{C}_{12}\text{H}_{25}\text{OCH}_2\text{CH}_2\text{OC}_{12}\text{H}_{25}$ 52% (130°C, 10hrs)
- (9) $2\text{C}_{16}\text{H}_{33}\text{OCH}_2\text{Cl} \longrightarrow \text{C}_{16}\text{H}_{33}\text{OCH}_2\text{CH}_2\text{OC}_{16}\text{H}_{33}$ 50% (130°C, 3hrs)

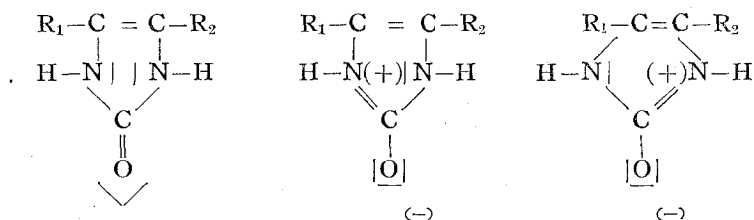
28. Studies on the Syntheses of Organic Fluorescent Compound. (I-II)

Ryohei Oda and Zen-ichi Yoshida

(Oda Laboratory)

I. Synthesis of Imidazolone Derivatives from Acylouins and Urea.

Imidazolone ring, which has a ethylene bond and a ureido group, resonates as follows:



It is considered accordingly, that ureido group is a kind of M substituent, and imidazolone ring has a favourable constitution on the emissivity of fluorescence from the present authors' theory concerning the fluorescence and chemical constitution of organic compounds.

As a matter of fact, 4,5-diphenylimidazolone, in which two phenyl groups are combined respectively with 4th and 5th positions of imidazolone ring, and the conjugation system is thus being enlarged, strongly fluoresces blue-violet rays in both solid and solution states under ultra-violet rays.

We synthesized several imidazolone derivatives and thioimidazolones.

As to the synthetic method we referred to Org. Synth. Collect. Vol. II. p. 222.

The yields are as follows: 4,5-diphenylimidazolone, Y=90%; 4,5-diphenylthioimidazolone, Y=57.8%; 4,5-bis (3,4-methylenedioxyphenyl) imidazolone, Y=40%; 4,5-bis (3,4-methylenedioxyphenyl) thioimidazolone, Y=37%; 4-phenyl-5-p-dimethylamino-phenylimidazolone, Y=76%.

4,5-Di-2-furylimidazolone wasn't obtained from froin and urea. This is due to the fact that froin decomposes itself in hot glacial acetic acid.

Fluorescence of 0.1% alcoholic solution of the diarylimidazolones under quartz lamp (3650A) was not so strong except that of 4,5-diphenylimidazolone. This may be due to the following reasons:

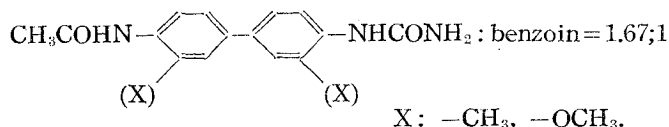
- 1). The polarity or the electronegativity of oxygen in $>C=O$ is larger than that of sulphur in $>C=S$, that is, +M effect of $>C=O$ is larger than that of $>C=S$.
- 2). The combined existing methylenedioxy group with 3rd and 4th positions of phenyl group makes the planar configuration of molecules difficult.
- 3). The combined existing dimethylamino group in p-position of phenyl group does not coincide with our theory.

II. Syntheses of Imidazolone Derivatives from Aromatic Ureides and Benzoin.

We synthesized polyarylimidazolones from several aromatic ureides and benzoin. Used ureides are as follows: Phenylurea, sym-diphenylurea, α -naphthylurea, 4'-acetylamino-4-ureidobiphenyl, 3,3'-dimethyl-4'-acetylamino-4-ureidobiphenyl, and 3,3'-dimethoxy-4'-acetylamino-4-ureidobiphenyl.

The synthetic method was nearly the same as in I, but the heating time was made longer than in I, and in the following ureides, mole ratio of starting substances was changed:

sym-diphenylurea: benzoin = 1:1



These polyarylimidazolones are substances whose hydrogens of imino groups in imidazolone ring were substituted by aryl groups such as phenyl, naphthyl and biphenyl. The yields were not so high as in the followings: 1,4,5-triphenylimidazolone, Y=21%; 1- α -naphthyl-4,5-diphenylimidazolone, Y=14%; 1,3,4,5-tetraphenylimidazolone, Y=12.2%; 4-(4,5-diphenylimidazolonyl (1))-4'-acetylamino-biphenyl, Y=30%; 3,3'-dimethyl-4-(4,5-diphenylimidazolonyl (1))-4'-acetyl-aminobiphenyl, Y=13.7%; 3,3'-dimethoxy-4-(4,5-diphenylimidazolonyl (1))-4'-acetylamino-biphenyl, Y=10.7%.

The synthesized polyarylimidazolones fluoresce blue-violet~greenish blue in alcoholic solution (0.1%) under quartz lamp (3650A). The observed emission intensity of fluorescence of these compounds showed to decrease as the number of substituents increased and as the aryl group became larger.